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The Effect of Cr_2O_3 as a Nucleating Agent in Iron-rich Glass-ceramics

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Abstract

In this work, the effect of Cr_2O_3 as a nucleating agent, in iron rich glasses has been investigated by means of DTA, XRD and density measurements. By Cr_2O_3 addition, from 0·4 to 1·0 wt%, a lowering of the crystallisation peak temperature resulted in the DTA trace, the maximum effect corresponding to 0·7 wt%. By evaluating the degree of crystallisation of the glass at 0·7 wt% Cr_2O_3, the highest efficiency in the nucleation process also corresponds. The optimum values for the nucleation and crystallisation time and temperature, determined for 0·7 wt% Cr_2O_3 addition, have been 70 min at 630°C and 30 min at 800°C. The crystalline phases formed at different thermal treatment temperatures of the parent glass have been investigated by XRD; the spinel is the only phase after the nucleation; pyroxene is the major phase after the crystallisation. The results of this study have highlighted that a small percentage of Cr_2O_3 strongly affects the spinel formation thereby reducing the time and temperature of the thermal treatment and enhancing the degree of crystallisation of high iron content glasses. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: glass-ceramics, Cr_2O_3, nucleation, crystallisation.

1 Introduction

Glasses with a suitable composition can be transformed into glass-ceramics by means of a thermal treatment, usually a two-step heating process. As a result, the parent glass is transformed into a composite material in which the crystalline phase is bonded by the residual glass so that different and sometimes outstanding properties are achieved.

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The first step of the heat treatment, at a lower temperature, is connected with the formation of heterogeneous nuclei, i.e. small crystallites with a size of about 100–1000 Å[1–3] promoting the growth of the major crystal phase. The higher the number of nuclei formed, the finer the structure of the glass-ceramics and the better the properties of the material.

The qualities of a glass-ceramic, however, depend on the kind and quantity of the crystal phase formed, as well as on the residual glass composition. In principle, the kind of crystal phase is related to the parent glass composition, but its quantity depends on the temperature and the time of the heat treatment. Therefore, the presence of an efficient nucleating agent in the correct concentration and the determination of the temperature and time of the nucleation and growth acquire particular importance in the formation of a glass-ceramic.

The nucleation process is usually investigated by two-step isothermal heat treatments. The first step corresponds to the temperature region of the nuclei formation and the second is at a higher temperature, where the nucleation rate is negligible but the crystals grow to a measurable size. Then, the nucleation efficiency can be estimated by microscopic methods[1] or by evaluating the degrees of crystallisation.[3,4] The higher the crystallisation the more efficient the nucleation step.

A further indication of the nucleation can be obtained by DTA technique because the formation of a consistent number of nuclei shifts the exothermic peak to a lower temperature.[5–8] Therefore an evaluation of the nucleation can be obtained by comparing the position of the exothermic peak in samples nucleated with a different thermal schedule.

The amount of crystal phase formed, as a result of the second stage heat-treatment, is generally estimated by an XRD analysis,[2,9] electron microscopy[1,2] or other techniques.[3,10] In a previous

paper[11] we reported the possibility of evaluating the degree of crystallisation in iron-rich glasses by simply measuring the variation of density between the parent glass and the glass-ceramic.

In the present paper, the effect of Cr_2O_3 as a nucleating agent is investigated in iron-rich compositions. This oxide is characterised by a low solubility in silicate melts, resulting in the direct formation of Cr-based spinels, which then appear as nuclei for pyroxene glass-ceramics.[4,12,13] It must be noted that the Fe–Cr spinel formation, investigated in this work, is somehow different from the formation of the magnetite spinel in similar compositions.[14–18]

In our experiments, a series of glasses with different Cr_2O_3 concentration ranging from 0 to 1·0 wt% were melted and the Cr_2O_3 effect as a nucleating agent was estimated by DTA and density variation. By using the same techniques, the nucleation and crystallisation temperatures and times were also evaluated.

2 Experimental

Glasses with the following compositions: SiO_2; 50·0, Al_2O_3; 3·8, Fe_2O_3; 24·8, CaO; 11·6, MgO; 0·3, ZnO; 2·8, PbO; 1·8, Na_2O; 3·9, K_2O; 1·0, were prepared by mixing jarosite, a zinc hydrometallurgy waste,[19,20] granite mud, a waste arising from the cutting of the blocks, sand, limestone, Na_2CO_3. The base composition was labelled as CR00. A 0·4, 0·7 and 1·0 wt% Cr_2O_3 was added and the corresponding glass compositions were indicated as CR04, CR07 and CR10, respectively. In order to increase the Fe^{2+}/Fe^{3+} ratio in the glass, a 3% carbon powder was added to each batch.

The melting was carried out in a super-kanthal furnace at 1450°C for 2 h utilising corundum crucibles. Glass samples were obtained by casting the molten glass on a stainless steel mould.

The crystallisation process was investigated by DTA technique, employing a Netzsch STA 409 apparatus. In each experiment, about 120 mg of a bulk sample was used at a heating rate of 15°C min^{-1}. A bulk sample was preferred to a powder one, in order to minimise the effect of the surface oxidation of Fe^{2+}.[21] Isothermal treatments were carried out with different thermal schedules and the degree of crystallisation was determined by evaluating the changes of density.[11] For this set of measurements, an AccyPyc 1330 He displacement pycnometer was employed. Using annealed bulk samples weighing approximately 3–4 g, the error associated to each measurement was evaluated as 0·001 g cm^{-3}.

The crystalline phases formed during the thermal treatments were determined by XRD technique, using a Philips PW-1830 apparatus and CuK_α radiation.

3 Results and Discussion

Figure 1 shows the DTA traces of CR00 and CR07 glass samples, respectively. The figure highlights a sensible shift of the exothermic peak, about 50°C, when Cr_2O_3 is present in the glass. Figure 2 reports the crystallisation peak temperature (T_p) for CR00, taken as the reference, and for CR04, CR07 and CR10 glasses, respectively. From the behaviour of the curve, it is evident that, for 0·7% Cr_2O_3 concentration, the lowest crystallisation temperature is obtained.

In order to determine the optimal temperature for the nucleation, CR07 samples were heat-treated for 60 min at 616, 623, 630, 636 and 643°C temperatures, i.e. the temperature region between T_g and $T_g + 50$°C, which is typical for nucleation.[12] DTA were carried out and the shift of the exothermic peak between the non heat-treated and the thermally treated samples (ΔT_p) was recorded and related to the nucleation step temperature. Figure 3 shows the DTA traces of the non nucleated and heat treated at 630°C CR07 samples, while in

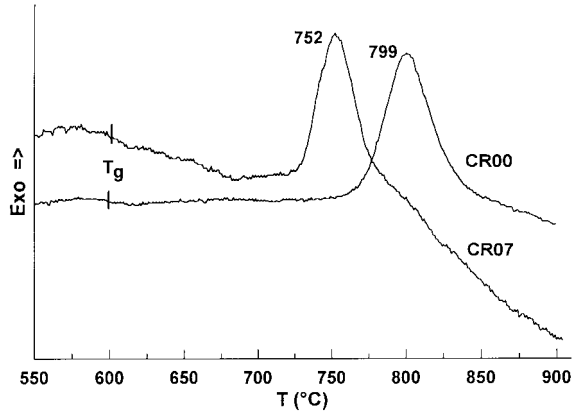

Fig. 1. DTA of CR00 and CR07 glass samples.

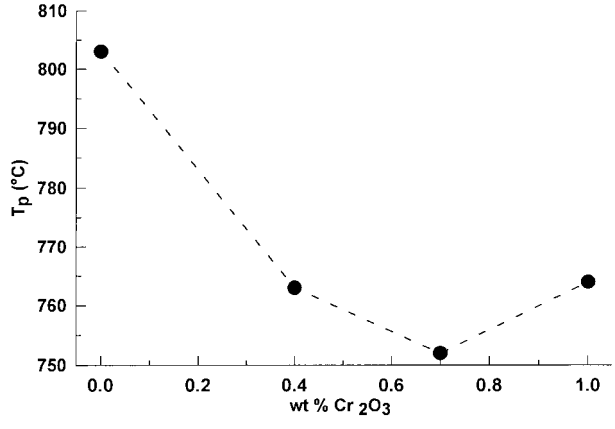

Fig. 2. Peak temperature versus wt% Cr_2O_3 percentage.

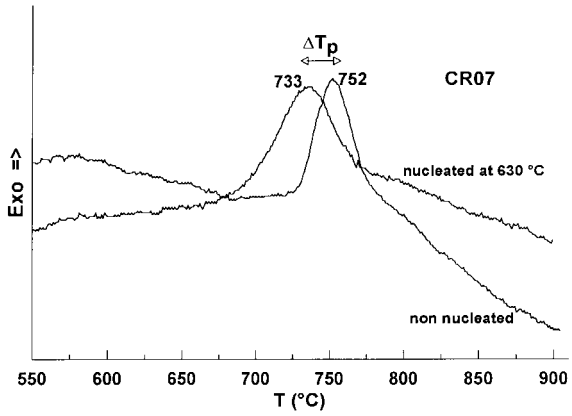

Fig. 3. DTA of nucleated and non nucleated CR07 glass samples.

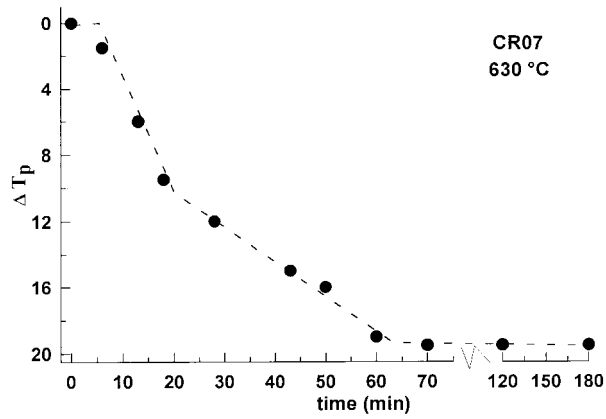

Fig. 5. Shift of the crystallisation peak ($\Delta\ T_p$) versus the nucleation time.

Fig. 4, the ΔT_p is plotted as a function of the nucleation temperature, T_n. For CR07 composition the plot highlights that the best nucleation temperature is about 630°C.

A similar behaviour was also shown by CR04 and CR10 glasses nucleated for 60 min at 630°C. The CR00, treated with the same thermal schedule, did not show any translation in the exothermic peak.

The optimal nucleation time was determined by plotting the ΔT_p as a function of the thermal treatment time, at 630°C. In this series of experiments, the CR07 glass was employed and the results are shown in Fig. 5. From the figure it can be inferred that, at the investigated temperature, no treatments longer than 70 min are necessary in order to obtain an efficient nuclei formation in the bulk of the glass.

As reported elsewhere,[11] the degree of the phase formation, α, resulting from the crystallisation process, can be evaluated by using density measurements. In this methodological approach glass-ceramics were considered as composite materials made up of different crystal phases and a residual glass. The volume of a glass-ceramics is practically an additive function of the volumes of the vitreous and crystal phases so that the density of the glass-ceramic can be related to the percentage crystal phase. The following equation was obtained for the degree of transformation:

$$\alpha = \left[\left(\rho_{x\tau} - \rho_g\right)\rho_{x\mathrm{tot}}\right] / \left[\left(\rho_{x\mathrm{tot}} - \rho_g\right)\rho_{x\tau}\right] \qquad (1)$$

where ρ_g is the density of the initial glass, $\rho_{x\tau}$ is the density at time τ and $\rho_{x\mathrm{tot}}$ is the maximum density at the end of the crystallisation process.

The wt% crystal phase formed, x, can be evaluated through the relation:

$$x = 100\left(1/\rho_g - 1/\rho_{gc}\right) / \left(1/\rho_{gt} - 1/\rho_c\right) \qquad (2)$$

Here ρ_{gc} is the density of the glass-ceramic, ρ_c is the density of the crystal phase formed and ρ_{gt} is the density of a glass, having the same composition as the crystal phase formed.

The effect of the Cr_2O_3 concentration on the nucleation and crystallisation processes was investigated by heat treating samples of each composition for 120 min at 630°C and subsequently, for 30 min at 700°C; the degree of crystallisation was then evaluated by the density method. In other samples, the crystallisation time at 700°C was prolonged for as long as 600 min, in order to obtain the maximum degree of crystallisation. The results are listed in Table 1. For the four glasses investigated in this study, the table reports the initial glass densities, the density after the nucleation step, the density after 30 and 600 min at 700°C.

It has been previously demonstrated that in iron rich compositions, where the crystallisation leads to the formation of pyroxene solid solution and magnetite,the degree of crystallisation measured by density change coincides with XRD determinations.[11] Moreover, due to the high density difference between the parent glass and the glass-ceramic the density measurements allow the evaluation of the beginning of the crystallisation process, when the percentage of crystal phase is low.

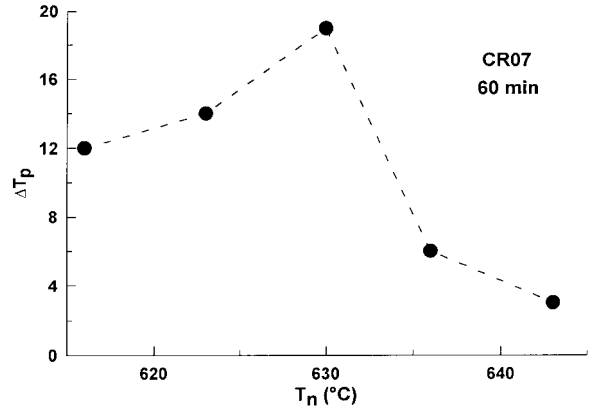

Fig. 4. Shift of the crystallisation peak ($\Delta\ T_p$) versus the nucleation temperature.

Table 1. Densities and corresponding percentages of crystal phase formed

% Cr_2O_3	Initial density ($g\ cm^{-3}$)	120 min at 630°C		30 min at 700°C		600 min at 700°C	
		($g\ cm^{-3}$)	wt%	($g\ cm^{-3}$)	wt%	($g\ cm^{-3}$)	wt%
0	2·891	2·893	—	2·955	12·9	3·042	29·6
0·4	2·896	2·903	1·9	3·036	27·4	3·078	35·2
0·7	2·904	2·915	2·9	3·071	32·1	3·103	37·9
1·0	2·900	2·905	1·7	3·054	29·9	3·095	37·4

The degree of conversion obtained after 30 min of heat treatment at 700°C, (α_{30}), calculated using eqn (1) and assuming as maximum degree of crystallisation the values obtained after 600 min thermal treatment at 700°C, is shown in Fig. 6 as a function of the Cr_2O_3 concentration. The figure highlights that the CR07 glass gives the highest rate of crystallisation.

The final series of experiments on the Cr_2O_3 concentration effect on the crystallisation processes, was carried out by thermally treating CR00 and CR07 samples in isothermal conditions in the 650–900°C temperature range. In performing these measurements, the samples were put into the oven and crystallised at 20, 40 and 60 min intervals; the density of each sample was then measured and plotted as a function of the temperature. The results are shown in Fig. 7 and suggest the following considerations:

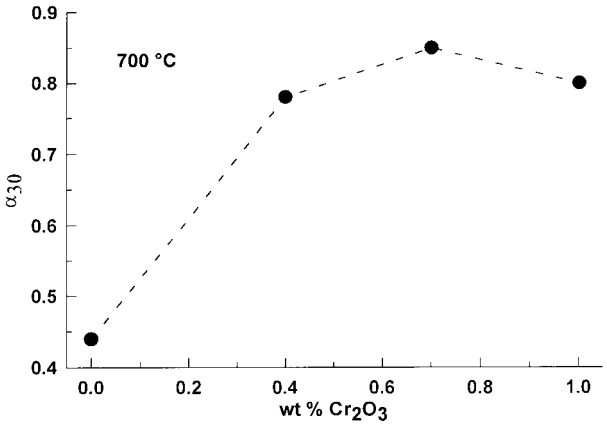

Fig. 6. Degree of transformation as a function of Cr_2O_3 percentage.

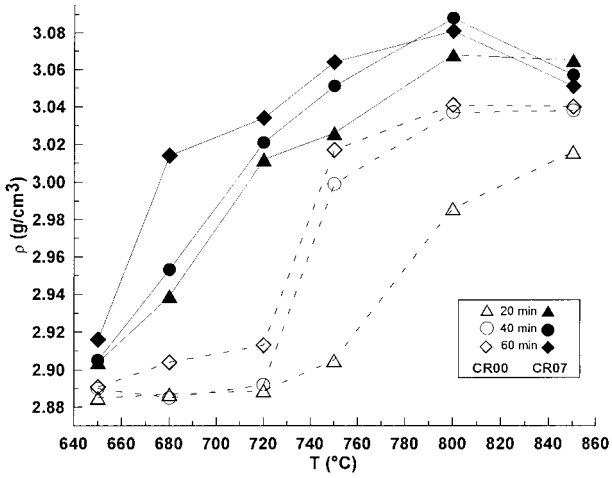

Fig. 7. Density variation of crystallised glass samples as a function of thermal treatment time.

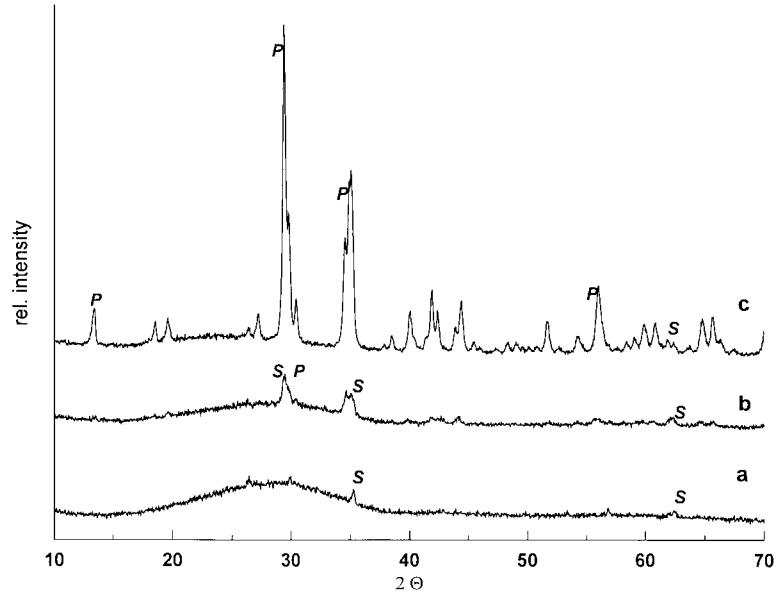

Fig. 8. XRD spectra of (a) initial glass, (b) nucleated sample (c) glass-ceramic.

- The CR00 glass starts the crystallisation at a temperature always above 720°C while, for the CR07 glass the crystallisation rate increases constantly as a function of the temperature up to 800°C due to the nuclei formation at low temperature. Above this temperature, a decreasing of the amount crystal phase is observed, due to the higher liquid/solid equilibrium ratio. Similar behaviour was also reported for other iron rich compositions.[17,18]
- The density of the CR07 samples, i.e. the degree of crystallisation, is always higher than the corresponding CR00 samples treated at the same temperature and time.
- The effect of time is negligible for CR07 glass and becomes irrelevant at temperature above 750°C, so that a 30 min second heat treatment at 800°C is proposed.

This study was concluded with XRD analysis of the crystalline phases formed by heat treatment of the CR07 glass. In Fig. 7, the parent glass (a) shows an amorphous spectrum with faint traces of spinel formation. After 120 min at 630°C the intensity of spinel crystals increases up to about 4 wt% (b); the beginning of pyroxene formation is also evident in the spectrum. The intensity of the peaks in the spectrum of the glass-ceramics, obtained after 70 min at 630°C and 30 min at 800°C corresponds to about 40–45 wt. % of pyroxene (c). The intensity of the spinel peak does not noticeably increase.

4 Conclusions

The results of this study highlighted the strong effect of Cr_2O_3 as a nucleating agent in high iron content glasses. The Cr_2O_3 addition, in percentages as high as 0·7%, enhances the spinel formation therefore increasing the number of nuclei available for crystallisation; as a result, a higher degree of crystallisation and a finer structure of the glass-ceramic are achieved.

The optimum values for the nucleation and crystallisation time and temperature resulted in being 70 min at 630°C and 30 min at 800°C, respectively. The spinels were the only phases formed during the nucleation; pyroxene was the major phase after the crystallisation with an average degree at about 40–45 wt%.

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